PB86-194503

Performance Audit of Inspection and Maintenance Calibration Gases

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

May 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-194503

EPA/600/D-86/101
May 1986

PERFORMANCE AUDIT OF INSPECTION AND MAINTENANCE CALIBRATION GASES

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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/D-86/101		

4. TITLE AND SUBTITLE	5. REPORT DATE
Performance Audit of Inspection and Maintenance Calibration Gases	May 1986
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Robert S. Wright (1), Clifford E. Decker (1), and William F. Barnard (2)	RTI/3180/18-01

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
(1) Research Triangle Institute, P.O. Box 12194 Research Triangle Park, NC 27709 (2) U.S. Environmental Protection Agency, MD 77-B Research Triangle Park, NC 27711	11. CONTRACT/GRANT NO. 68-02-4125

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency Office of Research and Development Environmental Monitoring Systems Laboratory Research Triangle Park, NC 27711	meeting paper
	14. SPONSORING AGENCY CODE EPA/600/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The purpose of the audit was to determine the accuracy of inspection and maintenance calibration gases for motor vehicle emission analyzers. Cylinders containing approximately 1.6 percent carbon monoxide and 640 parts per million propane in nitrogen were purchased from 13 specialty gas producers in 1984. Only three producers were able to provide cylinders that had been named according to the EPA Recommended Practice. RTI analyzed these gases in triplicate, using a gas chromatograph with flame ionization or thermal conductivity detectors. NBS Standard Reference Materials were used as reference standards for the analyses. Twelve of the 13 certified carbon monoxide concentrations were accurate to within plus or minus two percent relative. Nine of the 13 certified propane concentrations were accurate to within plus or minus two percent relative. Eleven of the 13 propane purities were greater than 99.0 percent. Confirmatory analyses at two EPA laboratories showed good agreement with RTI's analyses.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Quality Assurance Gas Mixture/Calibration Standard Automobile Exhaust Emissions Inspection & Maintenance Performance Audit Propane, Hydrocarbons Carbon Monoxide		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to public	unclassified	15
	20. SECURITY CLASS (This page)	22. PRICE
	unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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Introduction

One of the provisions of the Clean Air Act Amendments of 1977 is the implementation of motor vehicle emissions inspection and maintenance (I/M) programs for states or particular areas within a state that do not meet the National Ambient Air Quality Standard for carbon monoxide and/or ozone. The inspection function of an I/M program consists of the identification of those motor vehicles whose carbon monoxide and/or hydrocarbon tailpipe emissions exceed some specified limit. To accomplish this inspection function, analytical instrumentation must be used to measure the emissions and this instrumentation must be in accurate calibration at the time of the emissions measurement. The Environmental Protection Agency's (EPA's) Emission System Performance Warranty Regulations specify that the instrumentation must be calibrated with gas traceable to National Bureau of Standards (NBS) standards to within plus or minus two percent within a week of the emissions measurements (1).

EPA has established a recommended practice for naming I/M calibration gas (2, 3). This practice presents a set of procedures that specialty gas producers can use to blend, analyze and label calibration gases for non-dispersive infrared inspection analyzers used in I/M programs. Using the practice, producers should be able to attain the plus or minus two percent accuracy specification. If the producers use more stringent analytical tolerances than are specified in the recommended practice, they may certify an I/M calibration gas to an accuracy better than plus or minus two percent. The publication states in a section titled "EPA Audits:"

> EPA does not think it is necessary to check samples of a batch of calibration gas named according to the Recommended Practice prior to the sale and delivery of cylinders of the batch. However, EPA may from time-to-time order gas mixtures named according to the Recommended Practice from manufacturers through a third party for audit purposes. The results of such audits are likely to be published for public inspection.

This paper presents the results of a performance audit of I/M calibrations gases which were prepared and analyzed by 13 specialty gas producers. A list of these producers and their plant locations is given in Table 1. The I/M calibration gases were ordered with a requested carbon monoxide concentration of 1.6 percent and a requested propane concentration of 640 parts per million (ppm). They were purchased in October, 1984 by Research Triangle Institute (RTI) through an anonymous third party who did not reveal to the producers that the gases would be audited. This approach was used to assure that the gases were of typical quality.

The third party attempted to order calibration gases that had been named according to the recommended practice and that was traceable to NBS to within plus or minus one percent accuracy (i.e., with more stringent analytical tolerances than are specified in the recommended practice). In many cases, the producer was not familiar with the recommended practice, could not certify the I/M calibration gas to plus or minus one percent accuracy, or did not have NBS Standard Reference Materials (SRMs) on hand to use in the analysis of the I/M calibration gas. In these cases, the third party was directed to purchase the most accurate I/M calibration gas that each producer could provide. The certified traceability and accuracy of each gas is also listed in Table 1.

Three of the 13 gases were purchased as I/M calibration gases, named according to the recommended practice. However, neither the analytical certificates nor the cylinder tags for these three gases explicitly stated that they had been named according to the recommended practice. Such labeling and documentation is required by the recommended practice. Three other gases were purchased as EPA Protocol Gases. The certificates for two of these gases explicitly stated that they were EPA Protocol Gases, and one did not. The certificates for the remaining gases exhibited substantial variation in their levels of documentation regarding accuracy and traceability. The prices of the gases ranged between $125 and $430, with the mean price being $253. Aluminum cylinders were ordered from those producers who had them available. If an aluminum cylinder was not available, the producer's usual cylinder material was ordered. The cylinder materials for the I/M calibration gases are listed in Table 1.

Audit Procedure

After the I/M calibration gases were received by the third party, they were sent to RTI for analysis of their carbon monoxide, propane, and impurity hydrocarbon concentrations. After RTI completed its analysis, eight of the 13 gases were sent for confirmatory analyses at EPA's Standards Laboratory in Research Triangle Park (RTP), North Carolina, and at EPA's Facility Support Branch in Ann Arbor (AA), Michigan. At the EPA laboratories, the gases' carbon monoxide and total hydrocarbon concentrations were analyzed.

The basic measurement procedure that was used in RTI's analyses of the I/M calibration gases is the same as was used in a recent performance audit of EPA Protocol Gases (4). The reference standards for the measurements were two SRMs containing either propane in nitrogen (490 and 974 ppm) or carbon monoxide in nitrogen (0.96 and 1.96 percent). The propane and carbon monoxide instruments' linearities were determined by separate measurements of additional SRMs. This procedure differs from the recommended practice in that the calibration curve is established as a straight line between the two reference standards rather than the six reference standards specified in the practice.

Another difference is that the analytical instrumentation is calibrated "on the fly," rather than by the specified monthly calibration check. The cylinders were analyzed without dilution, in groups of six, including the two reference standards and four I/M calibration gases. These cylinders were connected to the analytical instrumentation by a sampling manifold, having solenoid valves controlled by a Lindberg Enterprises Model DL-W8 digital timer. The timer cycled through the group of six cylinders at least three times. As a result, each measurement of an I/M calibration gas was preceded and followed by measurements of the two reference standards. The instruments' calibration equation was recalculated for each I/M calibration gas measurement by linear interpolation between the two sets of reference standard measurements, and thereby is corrected for any short-term calibration drift.

Carbon monoxide was measured at RTI using a Perkin-Elmer Model 3920B gas chromatograph with a thermal conductivity detector and two 20-foot-long Molecular Sieve 5A columns. The sample value was controlled by the digital timer and injected at 4-minute intervals. The peak areas were integrated using a Spectra-Physics Model 23000 Integrator. Each carbon monoxide measurement consisted of five injections, of which the last three were averaged to yield mean carbon monoxide area counts. Three carbon monoxide measurements were obtained for each I/M calibration gas and were averaged to yield a mean carbon monoxide concentration.

Propane and impurity hydrocarbons were measured at RTI, using the same gas chromatograph with a flame ionization detector and a two-meter-long Durapak n-octane on Poracil C column. The sample valve was controlled by a Carle Model 4300 Valve actuator and a Carle Valveminder II, and injected at three-minute intervals. Each hydrocarbon measurement consisted of five injections, of which the last three were averaged to yield mean propane area counts and mean impurity hydrocarbon area counts. Three hydrocarbon measurements were obtained for each I/M calibration gas and were averaged to yield a mean propane concentration and a mean impurity hydrocarbon concentration. The Durapak column allowed propane to be separated from any impurities but did not allow the impurities to be identified. At a later date, selected I/M calibration gases were reanalyzed using a 23-percent SP-1700 on Supelcoport P-AW column, which allowed the impurities to be identified by species.

The precision of RTI's measurements is estimated by the coefficient of variation for multiple measurements of the same cylinder. The coefficients of variation for the carbon monoxide measurements range from 0.14 to 0.57 percent relative, with a mean of 0.33 percent relative. The coefficients of variation for the propane measurements range from 0.01 to 0.24 percent relative, with a mean of 0.14 percent relative.

At EPA-RTP, carbon monoxide was analyzed using a Bendix Model 8501-5CA non-dispersive, infrared carbon monoxide analyzer on its 0 to 1000 ppm range. A Bi-M digital static gas blender was used to dilute the I/M calibration gases such that the concentration of the resulting gas stream was within the analyzer's range. Three carbon monoxide in nitrogen SRMs were used as reference standards.

At EPA-RTP, total hydrocarbons were analyzed using a Beckman Model 400 hydrocarbon analyzer on its 0 to 100 ppm range. This instrument uses a flame ionization detector. A Bi-M digital static gas blender was used to dilute the I/M calibration gases such that the concentration of the resulting gas stream was within the analyzer's range. Two propane in air SRMs were used as the reference standards.

At EPA-AA, carbon monoxide was analyzed using an MSA Model 202 non-dispersive, infrared carbon monoxide analyzer on its 0 to 2.5 percent range. The I/M calibration gases were analyzed without dilution in groups of four. The reference standards were eight secondary standards, which had been named using gravimetric primary standards and NBS carbon monoxide SRMs. The results were displayed on a Fluke 4 1/2-digit digital multimeter and were manually entered into a computer, which calculated the measured concentrations. The analyzer's calibration curve was determined from a polynomial fit of the data from the eight reference standards.

At EPA-AA, total hydrocarbons were analyzed using a Beckman Model 400 Hydrocarbon Analyzer on its 0 to 1000 ppm range. This instrument uses a flame ionization detector. The I/M calibration gases were analyzed without dilution in groups of four. The reference standards were six secondary standards which had been named using gravimetric primary standards and NBS propane SRMs. The results were displayed on a Fluke 4 1/2-digit digital multimeter and were manually entered into a computer which calculated the measured concentrations. The analyzer's calibration curve was determined from a polynomial fit of the data from the six reference standards.

Audit Results

The results of the audit of the I/M calibration gases are given in Table 2. The accuracy of the producers' certified concentrations is defined as the absolute value of the percent difference between the producers' certified concentrations and RTI's corresponding measured concentrations. In general, the accuracy was quite good for carbon monoxide and was fair for propane. Shown below is a listing of the number of I/M calibration gases which fell into each of four ranges for the absolute value of the percent differences.

Absolute Value of Percent Difference	Number within Range	
	Carbon Monoxide	Propane
0 to 2	12	9
2 to 5	0	2
5 to 10	0	2
>10	1	0

The range of accuracies for the I/M calibration gases that had been named according to the recommended practice were approximately the same as for those that had not been named according to the recommended practice. For these three gases, the absolute value of the percent differences range between 0.0 and 1.0 percent relative for carbon monoxide and between 0.4 and 6.5 percent relative for propane.

As indicated in the previous section, impurity hydrocarbons concentrations were measured at the same time as were the propane concentrations. The impurity hydrocarbon concentration is the sum of all nonpropane peaks in the chromatogram. Measurement of both propane and impurity hydrocarbon concentrations allows the calculation of total hydrocarbon concentrations and propane purities. The total hydrocarbon concentrations are important because they are directly comparable with the EPA-RTP and EPA-AA results, whereas the propane concentrations are not directly comparable. The propane purities are important because the EPA Recommended Practice specifies:

> "...Propane or hexane must be 'instrument grade' which is certified to be 99.5 percent propane or hexane, and the balance will be primarily other hydrocarbons (e.g., methane, iso-butane, butane, and ethane). An analysis must be performed of this bulk propane or hexane to determine, in fact, that the gas used is at least 99.5 percent pure ..."

Impurity hydrocarbon and total hydrocarbon concentrations for the I/M calibration gases are presented in Table 3. The impurity hydrocarbon concentrations range between 1.7 and 17.0 ppm (measured as propane). Four of the 13 I/M calibration gases met the recommended practice's specification of 99.5 percent or greater propane purity. Seven of the 13 had propane purities between 99.0 and 99.5 percent. The remaining two had propane purities of 98.6 and 97.2 percent. The propane purities for the three I/M calibration gases named according to the recommended practice were 99.6, 99.5, and 97.2 percent. In general, these measurements suggest that the propane purities met or nearly met the recommended practice's specification for most of the I/M calibration gases.

At a later date, three of the I/M calibration gases were reanalyzed, using a different gas chromatographic column, in an attempt to identify the impurity hydrocarbons. In all three cases, the major impurity was identified as methane. The impurity concentrations were somewhat lower than were measured earlier. They ranged between 2.1 and 14.4 ppm (measured as propane), where they had previously ranged between 5.8 and 17.0 ppm.

The results of the confirmatory total hydrocarbon analyses at EPA-RTP and EPA-AA are given in Table 3. In general, there is good agreement beween the three sets of measurements. The percent differences between EPA-RTP's values and RTI's values range from -1.8 to -0.5 percent relative, with a mean of -1.4 percent relative. The percent differences between EPA-AA's values and RTI's values range from -0.6 to 0.2 percent relative, with a mean of -0.3 percent relative. Both EPA laboratories confirmed RTI's measurements for the four cylinders whose certified propane concentrations were inaccurate by more than 3 percent relative.

The results of the confirmatory carbon monoxide analyses at EPA-RTP and EPA-AA are given in Table 4. In general, there is excellent agreement between the three sets of measurements. The percent differences between EPA-RTP's values and RTI's values range from 0.2 to 1.4 percent relative, with a mean of 0.7 percent relative. The percent differences between EPA-AA's values and RTI's values range from -0.4 to 0.4 percent relative, with a mean of -0.1 percent relative. Both EPA laboratories confirmed RTI's measurement for one cylinder whose certified carbon monoxide concentration was inaccurate by 11.2 percent relative.

Findings and Conclusions

The performance audit of I/M calibration gases found that 12 of 13 certified carbon monoxide concentrations were accurate to within plus or minus 2 percent relative, and that 9 of 13 certified propane concentrations were accurate to within plus or minus 2 percent relative. Confirmatory analyses at two EPA laboratories showed good agreement with RTI's analyses. Eleven of the 13 propane purities were greater than 99.0 percent. Only 3 of the 13 specialty gas producers were able to provide cylinders that had been named according to the EPA recommended practice. In general, this audit indicates that specialty gas producers can prepare and analyze I/M calibration gases with reasonable accuracy for use in the emission control system performance warranty short tests.

Acknowledgements

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer review and administrative review policies and has been approved for presentation and publication. The research described in this paper has been wholly funded by the U.S. Environmental Protection Agency through Contract No. 68-02-4125 to Research Triangle Institute. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

The technical assistance and advice of EPA's Office of Mobile Sources, Emission Control Technology Division in Ann Arbor, Michigan is acknowledged. The excellent analytical work done by Avis P. Hines of EPA's Standards Laboratory, Quality Assurance Division, Environmental Monitoring Systems Laboratory in Research Triangle Park and by Gordon Becker of EPA's Facility Support Branch in Ann Arbor is appreciated. The technical assistance provided by the anonymous third-party is also appreciated.

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Table I. Specialty gas producers included in the audit of I/M calibration gases.

Specialty Gas Producer	Plant Location	Certified Traceability	Certified Accuracy	Cylinder Material
AGA Burdox	Maumee, Ohio	Recommended	1%	Steel
Airco Industrial Gases	Research Triangle Park, North Carolina	Protocol	1%	Aluminum
Air Products and Chemicals	Chicago, Illinois	Gravimetric	1%	Aluminum
Air Quality Products	Orange, California	California	1%	Disposable
Big Three Industries	Houston, Texas	CO SRM	1%	Aluminum
Ideal Gas Products	Edison, New Jersey	Primary	2%	Aluminum
Liquid Carbonic	Harrison, New Jersey	Protocol	--	Steel
Matheson Gas Products	Morrow, Georgia	Gravimetric	1%	Aluminum
MG Industries	North Branch, New Jersey	Recommended	1%	Aluminum
Scientific Gas Products	South Plainfield, New Jersey	---	10 ppm CO, 1 ppm C_3H_8	Aluminum
Scott-Marrin	Riverside, California	Protocol	1%	Aluminum
Scott Specialty Gases	Plumsteadville, Pennsylvania	Recommended	1%	Aluminum
Union Carbide	Warren, Michigan	SRMs	1%	Steel

Recommended = EPA Recommended Practice for Naming I/M Calibration Gases
Protocol = EPA Traceability Protocols Nos. 1 or 2
Gravimetric = National Bureau of Standards Gravimetric Standards
SRM = National Bureau of Standards Gaseous Standard Reference Materials
Disposable = DOT 39NRC-260 disposable steel cylinder
California = California Bureau of Automotive Repair master standard gas
Primary = Producer's accuracy designation

Table II. Summary of results from audit of I/M calibration gases.

Specialty Gas Producer	Carbon Monoxide Conc. (percent)			Propane Conc. (ppm)		
	Producer Certified	RTI Measured	Percent Difference[a]	Producer Certified	RTI Measured	Percent Difference[a]
AGA Burdox	1.598	1.582	1.0	639.0	600.2	6.5
Airco	1.45	1.633	-11.2	699	672.6	3.9
Air Products	1.58	1.564	1.0	647	637.3	1.5
Air Qual. Prod.	1.594	1.611	-1.1	640	643.9	-0.6
Big Three	1.62	1.618	0.1	660	618.4	6.7
Ideal Gas	1.68	1.658	1.3	636	664.8	-4.3
Liquid Carb.	1.59	1.582	-0.1	649	660.9	-1.8
Matheson	1.605	1.606	-0.1	639	651.4	-1.9
MG Industries	1.59	1.591	0.0	639	628.8	1.6
Sci. Gas Prod.	1.599	1.610	-0.7	637	631.9	0.8
Scott-Marrin	1.626	1.642	-1.0	655	654.2	0.1
Scott Specialty	1.612	1.620	-0.5	634.2	631.8	0.4
Union Carbide	1.60	1.609	-0.6	640	642.9	-0.5

[a] $$\text{Percent Difference} = 100\left[\frac{\text{Producer Conc.} - \text{RTI Conc.}}{\text{RTI Conc.}}\right]$$

Table III. Comparison of measured total hydrocarbon concentrations from audit of I/M calibration gases.

Specialty Gas Producer	RTI Measured (ppm)		EPA-RTP		EPA-Ann Arbor	
	Hydrocarbon Impurity[a]	Total Hydrocarbon	EPA Measured (ppm)	Percent Difference[b]	Measured (ppm)	Percent Difference[b]
AGA Burdox	17.0(c)	617.2	614	-0.5	616.1	-0.2
Airco	3.5	676.1	664	-1.8	673.8	-0.3
Air Products	3.7	641.0	---	---	---	---
Air Qual. Prod.	5.9	649.8	642	-1.2	651.2	0.2
Big Three	5.0	623.4	612	-1.8	621.4	-0.3
Ideal Gas	9.5(d)	674.3	663	-1.7	671.4	-0.4
Liquid Carb.	5.4	666.3	---	---	---	---
Matheson	2.5	653.9	643	-1.7	650.3	-0.6
MG Industries	2.8	631.6	625	-1.0	629.5	-0.3
Sci. Gas Prod.	1.7	633.6	---	---	---	---
Scott-Marrin	5.8(e)	660.0	650	-1.5	657.6	-0.4
Scott Specialty	3.8	635.5	---	---	---	---
Union Carbide	4.0	646.8	---	---	---	---
	Mean Percent Difference			-1.4		-0.3

[a]Hydrocarbon impurities were measured as propane.

[b] $$\text{Percent Difference} = 100 \left[\frac{\text{EPA Conc.} - \text{RTI Conc.}}{\text{RTI Conc.}} \right]$$

[c]Upon reanalysis, the impurity was identified as methane at a concentration of 14.4 ppm (measured as propane).

[d]Upon reanalysis, the impurity was identified as methane at a concentration of 6.6 ppm (measured as propane).

[e]Upon reanalysis, the impurities were identified as methane at a concentration of 1.4 ppm (measured as propane) and 0.7 ppm of a hydrocarbon longer in retention time than propane.

Table IV. Comparison of measured carbon monoxide concentrations from audit of I/M calibration gases.

Specialty Gas Producer	RTI Measured (Percent)	EPA-RTP EPA Measured (Percent)	EPA-RTP Percent Difference[a]	EPA-Ann Arbor EPA Measured (Percent)	EPA-Ann Arbor Percent Difference[a]
AGA Burdox	1.582	1.595	0.8	1.575	-0.4
Airco	1.633	1.641	0.5	1.630	-0.2
Air Qual. Prod.	1.611	1.633	1.4	1.618	0.4
Big Three	1.618	1.629	0.7	1.621	0.2
Ideal Gas	1.658	1.678	1.2	1.661	0.2
Matheson	1.606	1.610	0.2	1.601	-0.3
MG Industries	1.591	1.598	0.4	1.591	0.0
Scott-Marrin	1.642	1.648	0.4	1.636	-0.4
	Mean Percent Difference		0.7		-0.1

[a] $\text{Percent Difference} = 100 \left[\frac{\text{EPA Conc.} - \text{RTI Conc.}}{\text{RTI Conc.}} \right]$